THE USE OF FLUIDIZED BED COMBUSTER ASH IN THE SOLIDIFICATION OF HIGH OIL AND GREASE SEDIMENTS

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INTRODUCTION and BACKROUND

It has been common practice at petroleum refineries to dispose of oil sludges (containing oil, grease solids and water) in onsite pits. Remediation of these pits has typically involved in-situ solidification of the sludges using mixtures of Portland cement and fly ash. While this leaves the oily material in place, the resulting form is less permeable than the resulting sludge and has significant strength to support a cap. The supported cap reduces the infiltration rate of water to contact the solidified sludges. Due to the cumulative impact of the solidification and capping process the mobility of these materials is therefore reduced.

Since 1991 an oil refinery has been investigating the closure of several large storm water impoundment ponds. These ponds contain sediments that are high in oil and grease and mostly low in solids. Oil and grease content ranges from 1.5 to 20% by EPA Method 9071[1]. Consistencies and liquid content of the sediments vary from a very wet free flowing emulsion to a congealed sludge with about 70% solids. The primary concern of closure was to solidify the residues while still maintaining the low leachability and mobility of both metals and volatile organic hydrocarbons (VOCs).

During the project evaluation phase, a consulting engineering firm conducted a treatability study that evaluated Portland cement, cement kiln dust, Class C fly ash and pulverized quicklime for solidification of various pond sediment samples. The goal of this study was to develop formulations that would reduce the leachability of metals and VOCs below regulatory limits and obtain unconfined compressive strengths greater than 0.98 kilograms/sq.cm (Kg/sq.cm). The study's recommendations ranged from formulations with 20% Portland cement and 10% fly ash blend to formulations using 30 to 35% Portland cement. At these recommended cement loadings, the cost of the remediation was unacceptably very high. IT-Davy, a joint venture between IT Corporation and Davy Environmental, was hired to provide final engineering design and investigate lower cost solidification formulations. IT-Davy successfully demonstrated the use of by-product blends through field studies, a laboratory bench-scale confirmation study and a full-scale pilot demonstration.

<u>Preliminary Field Screening Studies</u>
Two stages of testing were performed in the field as a screening of reagents for later laboratory work. The first stage consisted of testing single reagents and blended reagents for strength development, rate of hardening, heat generation, and water absorption after hydration. Experiments consisted of testing 12 single reagents and 30 blends of these reagents. Reagents included four Class C fly ashes, five fluidized bed combuster ashes , two cement kiln dusts and Type 1 Portland cement.

The second screening stage consisted of mixing different single reagents and reagent blends that harden on hydration with a sediment sample (composited from several lagoons on the site) to achieve the highest strength. Seven of the more promising single reagents from the first stage that had good water adsorption, possible strength formation and low heats of reaction were mixed with a composite sediment sample in various dosages and measured for strength using development. Strength was measured by penetration resistance using a pocket penetrometer at seven days of cure. Various blended combinations of these reagents were then compared for strength using penetration resistance as measured by pocket penetrometer at seven days. These blends included cement/fly ash, cement kiln dust/fly ash, cement/fluidized bed combuster ash and mixtures of other by-products. Ratios of blend components were changed in increments of 20% to find the optimum mixture of reagents for the blend. The dosage of reagent blends was compared for formulations that met >1.0 Kg/sq.cm penetration resistance. Additional field screening was performed to optimize the reagent dosages of cement only and fly ash /fluidized bed combuster ash (FA/FBCA) blends.

Results showed that strengths could be achieved using cement or blends of fly ash and fluidized bed combuster ash at high dosages. Further testing was done on individual samples from each of the six lagoons on site (A, B, C, D, E, F). The percent solids and oil and grease content of these lagoons are found in Table 1. To increase the strength and lower the dosages, an absorptive soil was added to formulations with cement and FA/FBCA blend. The soil absorbed free water and thickened low solid sediments. With the addition of the soil, the strength criterion was increased to >3.0 Kg/sq. cm at seven days of cure increasing the oil retention of the formulations.

<u>Bench-Scale Confirmation Testing</u>
Four of the six lagoons were sampled and sediments were sent to IT's Environmental Technology Development Center in Oak Ridge, Tennessee for bench-scale testing. Sediment samples were designated A, B, C, D to identify the lagoon that they were taken. Using the results from the field screening, the

potential formulations shown in Table 2 were chosen for a bench-scale verification test. Two or three formulations were selected for each of four lagoon sample locations, labeled A, B, C, and D. Each location had varying amounts of solids, moisture, and oil and grease content. Percent solids and oil and grease are shown for all six lagoons are shown in Table 1. In most of the mixes, adsorptive soil was added to increase the solids content of the sediments. At all of the sample locations, formulations were tested using cement (as a control reagent for comparison) and the FA/FBCA blend. For samples A and B the formulations from the previous treatability study that used cement only or cement/fly ash blend without soil were made for comparison. Formulations were tested for the following:

- Unconfined compressive strength (UCS) at 3, 7, 28, 90 days measured by ASTM D2166-91[2]
- Permeability at seven days measured by ASTM D5084[3]
- Oil retention at seven days measured by liquid loss at 42 psi of compression for five minutes
- Sample cohesiveness in water after 14 days
- Volume increases
- Compliance with Toxicity Characteristic (TC) regulatory limits by analyzing the material using the Toxicity Characteristic Leachate Procedure (TCLP)[4]

Full-scale Demonstration

Successful FA/FBCA blend mix formulations were used in a full-scale in-situ pilot demonstration. A large area of a sediment pond was diked for this demonstration. Free standing water and oil were removed before the addition of fill soil and reagent. Various mixing and reagent addition techniques were explored. The optimized laboratory formulations were tested against various reduced reagent formulations to confirm dosage rates. Samples were taken to measure the success of the remediation. The goal was to confirm the strength of 1.4 Kg/sq.cm and permeability less than 1 x 10^{-5} cm/sec achieved during laboratory investigations. Test samples were made in 7.6 x 15.2 cm cylinders during daily production. Each was tested for UCS at 3, 7, and 28 days of cure. Permeability was tested at seven days.

RESULTS and DISCUSSION

Preliminary Field Screening Studies

The first stage of field reagent screening began by testing various possible cement substitutes for cement like properties of hardening, heat evolution, and water absorbtion. Water was added to various Class C fly ashes, fluidized bed combuster ashes and cement kiln dust. Portland cement was hydrated for comparison. Test results identified potential reagents from each group, but showed that the Class C ashes as a group performed most like cement.

Sediment formulations were then prepared using reagent dosages of 40 to 60 g per 100 g of sediment. Strength development was tested at seven days by penetration resistance. Of the 11 reagents, only one Class C fly ash and two FBCAs showed strengths over 1 Kg/sq.cm at seven days. However, at 40 to 60% loadings these could not compare favorably to cement loadings of 20%.

Cement and Class C fly ash blends from the earlier study were reevaluated. Ratios of cement to fly ash were varied in 20% increments. In all cases 7-day strength decreased as cement was replaced with fly ash. This test was repeated using FA/FBCA blends and gave similar results. In an attempt to eliminate the need for cement, cement kiln dust were blended with various Class C fly ash mixes using loadings up to 45%. None met the desired strength after seven days. The by-product blends were then evaluated using various fluidized bed comuster ashes with Class C fly ash. At specific ratios, these blends exhibited strengths almost equal to cement mixtures. The mix ratios of reagents were unique for each specific combination of by-products (ashes). Since the cost of the coal burner by-products was very low compared to cement, higher ratios of reagents could be used at a significant cost savings.

Similar formulations were made using fill soil as an absorbent and to increase the solids content of the mixture. Results revealed that reductions could be made in the loading of both single and blended reagents. The addition of soil allowed some previously unsuccessful blend combinations to show strengths above 3 Kg/sq.cm with greater oil retention. Even with the soil addition the use of cement kiln dust was not effective.

The reagents with the most potential were then tested at different soil to sediment and reagent loadings. Results are in Table 3.

These results confirmed that the addition of soil to absorb the excess oil and water and increase the solid content of the sediment would reduce the dosage rate for cement. Results also showed that when using an optimum soil to sediment ratio of 1 to 0.75 that the FA/FBCA performed as well as cement alone. Not only was the performance equal, but the reagent cost was reduced by 40% when using the FA/FBCA blend even at slightly higher dosages.

Final field treatability testing was performed using sediment samples from all six lagoons, bracketing the range of conditions on the site. Final mixes were made using two ratios of FA/FBCA in the dry blend that was mixed with the sediment.

The final field tests confirmed the previous test results. As a general trend using the reagent FA/FBCA blend at a high mix ratio, significant strength formed at lower dosages a lower blend ratio. Soil to sediment comparisons showed that the ratio of soil to sediment to get an acceptable compressive strength are dependent on the sample location. Since a lower ratio would reduce the bulking factor, the lowest ratio of soil to sediment was preferred. At the optimum soil ratio of 1:0.75 and at a high blend mix ratio a reagent dosage of 25% met strengths of >3 Kg/sq.cm for all sediment locations. These mix formulations were selected for the next phase, a controlled bench-scale verification study. These formulations are the subject of a patent application.

Bench-scale Verification Study

Sample formulations were made in two to three kilogram batches. Mixes were made using a Hobart mixer, with a spade shaped blade. The mix was placed into 5.1 x 10.2 cm cylindrical molds. Molds were allowed to cure in sealed containers at room temperature on the bench top. Bulk density was determined on the uncured mix by weighing the filled molds. No significant changes in volume of the mix occurred as the samples cured. Raw sample bulk densities varied from 1.07 g/cm^3 for the four sample locations. Grout mix densities for these sample varied from 1.2 to 1.6 g/cm^3.

Unconfined compressive strengths were tested by ASTM Method D2166 at 3, 7, 28, and 90 days. The passing criterion was >1.4 Kg/sq.cm at seven days of cure, which is based on developing enough strength to support construction equipment during the remediation phase of the project. No other specific criteria were established, but the total strength at 28 days of each sample were compared. See Table 4 for the UCS data. All the formulations using the FA/FBCA blend met the desired strengths. The cement formulations using soil were lower than the desired strength and the cement only formulations were much lower than the desired strength.

Sample molds were tested for permeability at seven days of cure by ASTM method D5084. Passing criteria was to have lower permeability than the permeability of the surrounding basin. The closure plan established 1 x 10^{-5} cm/sec as the passing goal. All of the tested formulations met this requirement.

Liquid retention capacity was tested at seven days of cure. Samples used to measure unconfined compressive strength were crushed and reworked by hand. This material was placed into a 3.6 cm diameter stainless steel Carver mold. The mold was configured with a porous bottom plate that was covered with a filter paper to separate the sample from the plate. The mold was filled with sample, manually compacted and a 3.0 Kg/sq.cm load was applied for 5 min. Liquid retention was measured as a percentage of the weight retained. All of the samples retained betwwen 89 and 96.6 % of thier total liquid content. The FA/FBCA blend formulations all retained over 95% of their weights. Values for the cement mixes were generally 5% lower. When the percent liquid retention wasgraphed against the unconfined compressive strength, the graph showed that retention values improve with increasing strength up to 1.8Kg/sq.cm.

The durability of 14 day cure samples was tested by submerging them in water. Blocks of solidified samples were immersed in beakers of water. Covers were placed on top to prevent evaporation. Results were recorded as visual observations. Cohesiveness, precipitation and oil sheen were noted. Observations were recorded over 90 days. These results show that slight oil sheens are present on all sample surfaces. In all cases the cement formulations exhibited more sheen than the FA/FBCA blend mixes. After two days the sheen was reduced in all beakers. White precipitate formed in cement mixes at two hours. At later time a smaller quantity of similar precipitate also formed in the by-product blend mixes. This precipitate is thought to be calcium hydroxide or calcium sulfate, by-products of cement hydration. No evidence of physical deterioration was seen in any of the samples. No changes occurred between nine and ninety days.

Samples were extracted at seven days using the TCLP method . The extracts were analyzed for semi-volatiles, volatiles and metals. No concentrations were expected above regulatory requirements because the original materials were within passing criteria. The leachability of the treated materials were all less than or equal to the leachabilities of the untreated sediments, and therefore below the TC regulatory criteria for these compounds.

The following recommendations were made from the bench-scale verification results:

- The FA/FBCA blend is an effective and economical replacement for cement in the stabilization of oily sediment.
- Absorbent fill soil is suitable for reducing reagent loading, while maintaining high strength, durability and low permeability.
- Controlling solids content is critical to effective solidification.
- Oil and grease in concentrations < 20% has little effect on the reagent dosages in the proposed mix designs.

The recommend mix designs are: 1) Removal of free water before solidification; 2) Use absorbent fill soil to obtain 55 to 60% solids content; and 3) Add 25 to 30% FA/FBCA blend.

Recommendations from bench-scale verification were used to design a full-scale in-situ pilot demonstration.

Full-scale In-situ Demonstration

The purpose of the pilot demonstration was to test the ability to use the laboratory designs in the field. Many operational performance goals were addressed in this study that are beyond the scope of this paper. The technical goals of strength, mixing and permeability will be addressed.

Before stabilization a large sediment basin was divided using several dikes. The demonstration area was then dewatered by pumping free liquid from above the sediment. Solids content was increased to between 55 and 60% using fill soil. A long-stick trackhoe was used to mix soil into the sediment. Blending took place over several days so that the moisture could be absorbed by the soil. Additional soil was added as determined by field moisture determinations. Reagents were added to the mixture by delivery using a pneumatic tanker. Mixing was by three different techniques: 1) Long-stick trackhoe blending; 2) In-situ rotary mixer blending; and 3) Bulldozer blending.

The first two methods were done in-situ while the bulldozer blending was done on a pad. Both the bulldozer and the trackhoe mix were of a satisfactory consistency. Rotary mixer blending was unsatisfactory due to entanglements of debris with the mixer and the consistency of the mixes.

Variations in mix formulations were made to test the criticality of percent solids and reagent dosages. Samples were taken during mixing to be tested for compressive strength and permeability. Samples were aged in sealed containers on laboratory bench top separate from the remediation areas. Table 5 contains soil sediment ratios, percent reagents, final percent solids, compressive strengths, and permeabilities. Mixes with above 55% solids before adding the by-product blend gave acceptable strengths above 1.4 Kg/sq.cm at seven days. Permeabilities for all mixes were below 1×10^{-5} cm/sec which is ten times greater than the permeability of the surrounding soil. These data show that field results are consistent with earlier field screening and bench scale verification data.

CONCLUSIONS

IT-Davy demonstrated that an alternative solidification reagent is available to stabilize sediment with oil and grease contents below 20%. When used at the proper solids content a FA/FBCA blend gave equal or better strength and permeability compared to Portland cement. Because the cost of these combined reagents is lower than cement, larger dosages can be used at a lower cost. The practicality of these reagents has been demonstrated by field screening, bench-scale verification and a full-scale in-situ demonstration.

REFERENCES

1 EPA Method 9071, "Oil and Grease Extraction Method for Sludge and Sediment Samples", Test Methods for Evaluating Solid Waste Physical/Chemical Methods SW 846, 3rd Ed. Vol 1C

2 ASTM D2166, "Test Method for Unconfined Compressive Strength of Cohesive Soils", American Society of Testing and Materials, 1991. Vol. 04.08

3 ASTM D5084, "Test Method for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter", American Society of Testing and Materials, 1991. Vol. 04.08

4 EPA Method 1311, "Toxicity Characterization Leaching Procedure", Test Methods for Evaluating Solid Waste Physical/Chemical Methods SW 846, 3rd Ed. Vol 1C

TABLE 1. PERCENT SOLIDS AND OIL AND GREASE FOR ALL SIX LAGOON SITES

SAMPLE LOCATION	% SOLIDS	% OIL and GREASE
A	20	6
B	35	12
C	29	11
D	20	11
E	46	11
F	67	20

TABLE 2. BENCH-SCALE VERIFICATION TEST FORMULATIONS

SAMPLE LOCATION	REAGENT	DOSAGE PER 100 g OF SEDIMENT	ABSORPTIVE SOIL PER 100 g OF SEDIMENT
A	PORTLAND CEMENT FA/FBCA BLEND PORTLAND CEMENT	17 30 25	125 125 0
B	PORTLAND CEMENT FA/FBCA BLEND CEMENT/FLY ASH BLEND	17 20 25	75 75 0
C	PORTLAND CEMENT FA/FBCA BLEND	22 30	75 75
D	PORTLAND CEMENT FA/FBCA BLEND	17 20	75 75

TABLE 3. PENETRATION RESISTANCE AT 7 DAYS (Kg/sq.cm)

SOIL/SEDIMENT (w/w)	DOSAGE PER 100 g OF SEDIMENT	PENETRATION RESISTANCE USING EACH REAGENT		
		TYPE I PORTLAND CEMENT	CLASS C FLY ASH	FA/FBCA BLEND (MID-LEVEL RATIO)*
1/1	10	1.6	-	0.4
1/1	15	4.0	0.1	1.5
1/1	20	-	0.2	2.5
1/0.75	15	3.0	-	3.1
1/0.75	20	3.5	-	4.2
1/0.75	25	-	0.5	>4.5
1/0.5	15	1.2	-	-
1/0.5	20	3.0	-	2.6
1/0.5	25	>4.5	0.3	3.4
1/0.5	30	-	1.3	>4.5

* Multiple ratios of FA/FBCA were investigated. These results are for the mid-level ratio blend of FA/FBCA.

TABLE 4. UNCONFINED COMPRESSIVE STRENGTH

SEDIMENT SAMPLE	MIX FORMULATION	UCS (kg/sq.cm) 3 DAYS	7 DAYS	28 DAYS	90 DAYS
A	Sed:Soil:Cement (100g:125g:17g)	0.35	0.42	0.84	0.98
	Sed:Soil:FA/FBCA Blend (100g:125g:30g)	1.62	3.52	4.29	4.71
	Sed:Cement (100g:25g)	ND	1.12	2.04	ND
B	Sed:Soil:Cement (100g:75g:17g)	0.84	1.34	1.90	2.81
	Sed:Soil:FA/FBCA Blend (100g:75g:20g)	0.56	1.62	1.97	2.53
	Sed:Cement/Fly ash (100g:25g)	ND	0.63	1.20	ND
C	Sed:Soil:Cement (100g:75g:22g)	0.14	0.14	0.21	0.28
	Sed:Soil:FA/FBCA Blend (100g:75g:30g)	0.77	2.95	4.22	4.71
D	Sed:Soil:Cement (100g:75g:17g)	1.12	1.62	2.39	2.95
	Sed:Soil:FA/FBCA Blend (100g:75g:20g)	0.63	1.76	2.25	2.53

TABLE 5. FULL-SCALE IN-SITU DEMONSTRATION DATA

	ISOLATION DIKE AREA		SOUTH DEMONSTRATION AREA				DOZER MIX AREA
	Cell No. 1	Cell No. 2	Cell No. 1	Cell No. 2	Cell No. 3	Cell No. 4	
Sediment to Soil Ratio	1:2.8	1:2.1	1:2.5	1:1.4	1:0.9	1:0.7	1:0.75
Percent Solids, Sediment and Soil	68%	65%	54%	53%	48%	45%	54%
Percent FA/FBCA Blend, by Wet Weight							
- Of Sediment	55%	42%	39%	29%	17%	14%	25%
- Of Sediment/Soil	14%	14%	16%	12%	9%	8%	17%
Final Mix, Percent Solids	72%	69%	60%	58%	52%	49%	60%
-Density, Kg/sq.cm	7.45	7.38	6.61	6.19	--	—	6.75
Compressive Strength, Kg/sq.cm							
- 3 days	0.70	0.70	0.42	0.28	Soft	Soft	Soft
- 7 days (ave. of 2)	1.69	2.04	1.27	0.28	Soft	Soft	—
- 28 days	4.50	3.30	2.18	1.41	Soft	Soft	—
Permeability, cm/sec x 10^{-7} - 7 days	—	1.6	1.7	1.6	—	—	5.7